

HALOGEN GEOCHEMISTRY (F, Cl, Br, I) AND Cl ISOTOPE COMPOSITIONS OF APOLLO RETURN SAMPLES. A. M. Gargano¹, Z. D. Sharp¹, C.K. Shearer², J. I. Simon³, and W. Buckley⁴, ¹Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, 87131 (agargano@unm.edu), ²Institute of Meteoritics, University of New Mexico, Albuquerque, 87131, ³Center for Isotope Cosmochemistry and Geochronology, ARES, NASA JSC, Houston, TX 77058, USA, ⁴Jacob-JETS Contract, NASA JSC, Houston, TX 77058, USA.

Introduction: The Moon is well recognized to exhibit a marked depletion in volatile elements relative to the Earth, due in-part from the Moon-forming impact, and the Lunar Magma Ocean [1, 2]. While the extent of volatile element depletion in the Moon is extensively debated, the common presence of volatile element stable isotope anomalies (i.e. Cl, Zn, H) in lunar materials is interpreted as the result of a significant loss of volatiles at some point in its formation history. Understanding the mechanisms and extent of this volatile-loss is important as the chemical evolution of planetary bodies towards conditions suitable for life likely requires the retention of some volatiles such as H, and the loss of others which can be toxic at high concentrations such as the halogens [3]. Gargano & Sharp (2019) recently showed that this latter process of Cl-devolatilization throughout the formation of the Earth accounts for a significant loss of Cl (>50%) and its higher $\delta^{37}\text{Cl}$ value of ~0‰ compared to those of iron meteorites which are interpreted to more closely represent the initial isotopic composition of the nebula (~ -7‰) [4]. Here, we build on this idea of halogen-loss as an important process in the evolution of habitable planetary bodies by exploring the systematics of halogen geochemistry in lunar materials. In this work we present the first comprehensive suite of halogen concentration data (F, Cl, Br and I) alongside bulk Cl-isotope measurements in planetary materials.

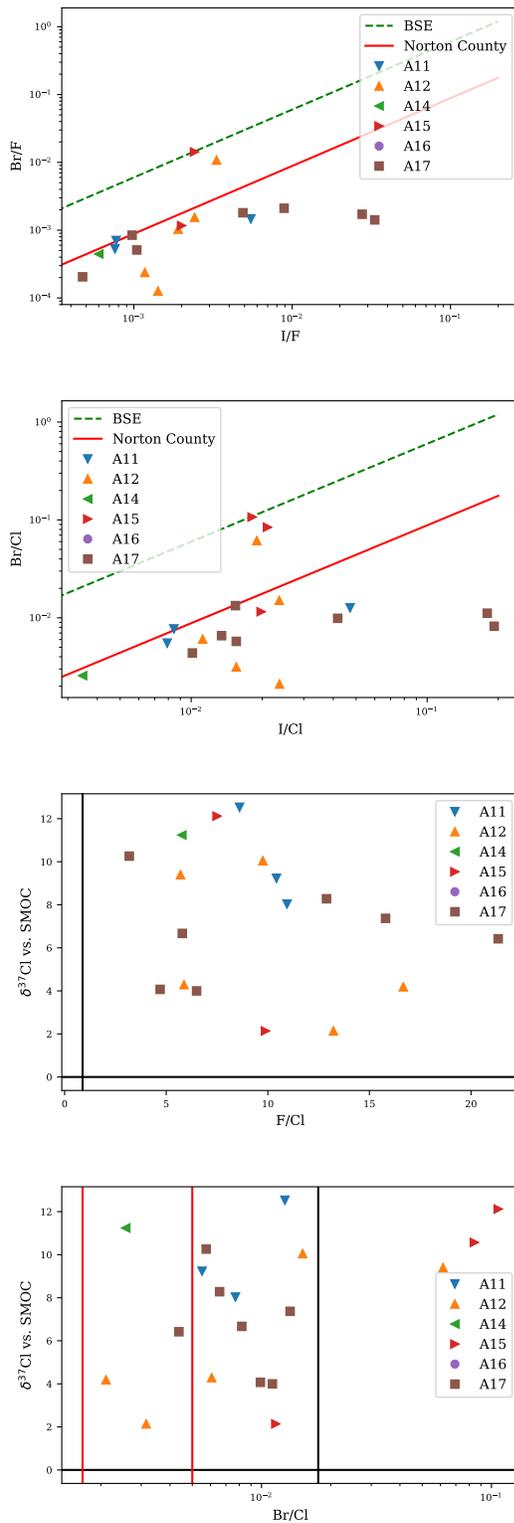
Background and Motivation: Lunar materials exhibit the largest ranges in $\delta^{37}\text{Cl}$ values in planetary materials measured both in bulk and in-situ measurements ranging from -0.7 to >30‰ [5-7]. The mechanisms thought to cause these heavy-isotope enrichments vary from anhydrous degassing of metal-chlorides, Cl degassing throughout crystallization of the LMO and degassing of urKREEP from crust-breaching impacts [5-7]. Regardless of the preferred volatilization mechanism attributed to producing the Cl isotope anomalies, the exceptionally high $\delta^{37}\text{Cl}$ values are necessarily explained by the preferential loss of the light Cl isotope (Cl^{35} relative to Cl^{37}). It is therefore expected that high $\delta^{37}\text{Cl}$ values should relate to lower Cl concentrations; however, this idea is inconsistent with the in-situ measurements of apatite which generally shows increasing $\delta^{37}\text{Cl}$ values with higher [Cl] and

other geochemical signatures indicative of urKREEP [6, 7]. One underlying assumption for the predicted anticorrelation is that all samples have the same initial [Cl]. We suggest that a more appropriate comparison is to use the ratios of geochemically similar halogens that differ significantly in their mass, avoiding the problem of variations in initial concentration.

In terrestrial igneous systems, it is thought that the Cl/Br/I ratios are effectively constant throughout igneous differentiation and degassing, whereas F is not efficiently lost by degassing [8, 9]. Additionally, Wang et al. (2014) have shown that the F/Cl ratio decreases throughout magmatic differentiation, and increases during degassing as Cl is efficiently degassed relative to F. Assuming that the geochemical behavior of Cl, Br and I are similar, we suspect that the large mass differences of these elements (i.e. $\text{Cl}^{35, 37}$, $\text{Br}^{79, 81}$, and I^{127}) should result in large elemental fractionations alongside increases in $\delta^{37}\text{Cl}$ values.

Methods: Samples were prepared following the methodology of Sharp et al. (2010) in which powders were melted via pyrohydrolysis. Sample solutions obtained by this method were then used for the following measurements: F by Ion Chromatography in the Analytical Chemistry Lab at UNM, Cl, Br and I concentrations were measured by ICPMS at the Center for Isotope Cosmochemistry and Geochronology at Johnson Space Center following the methodology of Bu et al. (2003), and Cl isotopes were measured at the Center for Stable Isotopes at UNM.

Results: The halogen concentrations in lunar materials are generally correlated with each other with some notable samples exhibiting uniquely high I and Br contents. F concentrations range from 4-40 ppm, and are the lowest in A17 norites and troctolites. Br concentrations range from 0.01-0.06 ppm with three Br-rich samples of around 0.14-0.16 ppm. Iodine concentrations largely range from 0.02-0.05 ppm with three samples showing uniquely high I contents of around 0.2-0.55 ppm. For a relative comparison, the BSE is thought to contain 15 ppm F, 17 ppm Cl, 0.3 ppm Br, and 0.05 ppm I [10].



Figures 1-4: 1, 2) I/F Vs. Br/F and I/Cl Vs. Br/Cl. Green dotted line shows the halogen ratios of the BSE [10]. Red solid line in Fig. 1 shows halogen ratios of Norton County

Aubrite also measured in this work. 3, 4) F/Cl Vs. $\delta^{37}\text{Cl}$, and Br/Cl Vs. $\delta^{37}\text{Cl}$. Intersection of thin black lines shows the halogen ratios and $\delta^{37}\text{Cl}$ value of the BSE [10]. The red lines span the range of Br/Cl ratios of terrestrial igneous rocks [8].

Discussion & Conclusion: The halogen ratios in lunar materials show a distinct trend and are off-set from the BSE, more closely resembling Norton County. This difference is driven by a depletion of nearly an order of magnitude in both [Br] and [I] in lunar materials relative to the BSE. The uniquely Br, and I-rich samples require an unknown mechanism of fractionating these elements from one another, as they are thought to be insensitive to magmatic differentiation and degassing [8, 9]. The F/Cl ratios are distinctly lower than the average MORB (~ 40) [11], and independent with $\delta^{37}\text{Cl}$ values, suggestive that the F/Cl ratio is largely driven by differentiation as opposed to degassing. The Br/Cl ratio spans a large range of nearly two orders of magnitude, whereas mantle-derived terrestrial rocks vary relatively little with Cl/Br ratios from between 200 and 600 (red lines in Fig. 4) which are thought to closely resemble their source reservoirs [9]. The large range in Br/Cl ratios in lunar materials therefore suggests that multiple reservoirs with distinct halogen ratios are measured in the Apollo suite. Additionally, although Br/Cl is thought to be insensitive to magmatic degassing on Earth, the significant mass differences of these elements holds the possibility that degassing into a vacuum as would be expected on the Moon could increase the Br/Cl ratio of a degassing magma reservoir. This model is generally consistent within individual sample suites (largely represented by mare basalts, with the exception of the A17 samples) which show increasing $\delta^{37}\text{Cl}$ values with Br/Cl.

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